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62448-TH

CATALYST COMPONENT AND CATALYST FOR THE (CO)POLYMERISATION OF
ETHYLENE, AND METHOD FOR THE PREPARATION THEREOF

FIELD OF INVENTION

The present invention relates to a dual site catalyst component comprising an inorganic support, a chromium oxide and a metallocene compound; and a catalyst comprising this catalyst component and an aluminoxan, and a method for the preparation of said catalyst component. In particular, the catalyst comprises a silica support, chromium oxide, a bis-cyclopentadiene zirconium or hafnium halide and an aluminoxan. The catalyst is particularly suitable for producing polyethylenes having a bimodal or broad molecular weight distribution.

PRIOR ART

Linear polyethylenes, such as high density polyethylene (HDPE) and linear low density polyethylene (LLDPE), can be endowed with specific properties through a suitable choice of polymerization conditions and polymerization catalysts, of which the chromium oxide and metallocene catalysts are among the commercially most important. Chromium oxide catalysts are characterized in that their active sites have different activities. As a result, the obtained polymer will have a possible comonomer and side chains unevenly distributed along the polymer backbone, mostly on the shorter chains of the matrix. Consequently, the produced polymers will have a broad molecular weight distribution, and these polymers will have good processability properties. The metallocene catalysts, often called single site catalysts (SSC) because all their active sites are equal, produces polymers having a narrow molecular weight distribution and an even distribution of possible comonomers and side chains along the polymer backbone. These polymers have desired properties like high impact strength, good transparency, and high hot tack. The main disadvantage is their poor processability due to the narrow molecular weight distribution.

> A combination of the properties of the chromium oxide and metallocene polymers would be highly desirable for many end uses, in particular will polyethylenes having a controlled broad or bimodal molecular weight distribution be advantageous in polymer processing by extrusion. Such polyethylenes have traditionally been produced by consecutive polymerisations at

different conditions in two reactors in a series. Another approach has been to perform the polymerisations in the presence of a modified catalyst, including the use of combinations of different catalysts. However, when combining different catalysts, such as chromium and metallocene containing catalysts, they have a tendency to inactivate each other.

US 3,378,536 discloses a process for the polymerization of ethylene by the use of a two-component catalyst system consisting of (a) chromium deposited on e.g. silica, where the chromium is activated in an oxygen-containing gas at a high temperature, and then reduced with CO; and (b) chromium or vanadium arene where the arene is an aromatic, optionally substituted, C_6 ring. The two catalyst components are preferably fed separately to the polymerization reactor.

EP 088 562 discloses a modified polymerization catalyst comprising a silica support with deposited chromium. Following oxidation in dry air, the chromium is modified by being contacted with a transition metal compound containing a π -bonded ligand. The transition metal is Ti, V or Cr, preferably Ti. Preferably, the ligand is an unsaturated carbocyclic or heterocyclic ring system containing 6 delocalized π -electrons, for example cyclopentadienyl. Only the use of bis-toluene titanium is exemplified, and the obtained polyethylenes have a substantial degree of branching and a medium broad molecular weight distribution.

US 5330950 and US 5408015 relate to ethylene polymers having broad molecular weight distributions, obtained by the use of a catalytic mixture including a MgO-supported Ziegler catalyst and a chromium oxide catalyst.

US 5399622 discloses a process for the polymerization of ethylene. The polymerization is started with a chromium oxide catalyst to obtain granules of low density polyethylene. The polymerization is continued by adding a cocatalyst and an yttrium-containing catalyst of formula $(Cp_2YX_n)_rM_sL_n$, wherein Cp is an

optionally substituted cyclopentadienyl, X is a halide, M is an alkali metal and L is an electron donor ligand, to obtain an outer shell of high density polyethylene on said granules.

NO 172,242 discloses a process for the production of polyethylenes having a broad molecular weight distribution. It is used a catalyst system consisting of: a catalyst component (A) comprising a silica support onto which there is deposited a titanium or chromium compound; a catalyst component (B) comprising a transition metal compound with a ligand having conjugated π -electrons e.g. Cp_2ZrCl_2 ; and a catalyst component (C) which is an aluminoxan, e.g. MAO. This catalyst system differs from the catalyst of the present invention by comprising three separate catalyst components, and by containing CrO_3 , not CrO .

EP-A-0 287 666 discloses a process for the polymerization of olefins in the presence of a catalyst composed of (A) a metallocene compound, e.g. Cp_2ZrCl_2 , optionally supported on silica, (B) an aluminoxan, and (C) an organoaluminium compound, e.g. triisobutyl aluminium. The obtained polymers have a narrow molecular weight distribution.

WO 96/14154 discloses a dual site catalyst comprising a calcined silica support impregnated with dibutylmagnesium, 1-butanol and TiCl_4 , and also impregnated with MAO and $(\text{BuCp})_2\text{ZrCl}_2$. This catalyst, which contains both a non-metallocene and a metallocene transition metal component, is used in the polymerisation of ethylene in one single reactor to obtain polyethylenes having a bimodal molecular weight distribution.

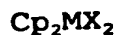
The object of the present invention is to provide a dual site catalyst that may be used in a single polymerisation reactor to obtain ethylene polymers having a controlled bimodal or broad molecular weight distribution. It has now surprisingly been found a versatile dual site catalyst that combines the features of both the prior art chromium oxide and metallocene catalysts. A remarkable advantage is that this catalyst produces chromium and SSC polyethylenes simultaneously in one and the same polymer

particle. The polymer particles as polymerised will when processed give a homogeneous polymer melt. Thus, the obtained polymer may be endowed with properties in the range from those obtained by using a chromium oxide catalyst alone to those obtained by using a metallocene catalyst alone. With this novel dual site catalyst polyethylene resins for a broad application area can be produced. The resins have particularly good extrusion properties and are especially well suited for processing by film blowing and blow moulding.

SUMMARY OF THE INVENTION

The present invention thus provides a catalyst component for the polymerisation of ethylene and ethylene with α -olefins, comprising:

- a) a support being a particulate inorganic oxide selected from the group comprising silica, alumina, and a combination thereof, said support having a particle size in the range of from 20 μm to 150 μm and a surface area from 200 to 600 m^2/g ;
- b) a chromium oxide in an amount of from 0.001 % to 10 % by weight calculated as chromium, based on the weight of the inorganic support; and
- c) a metallocene compound of formula:



wherein Cp is unsubstituted or substituted cyclopentadienyl, M is zirconium or hafnium, and X is a halide.

The present invention also provides a catalyst for the polymerisation of ethylene and ethylene with α -olefins, comprising the catalyst component defined above, and an aluminoxan as an activator.

A method for the preparation of the catalyst component defined above comprises the steps of:

- a) calcining a support being a particulate inorganic oxide selected from the group comprising alumina, silica and a combination thereof, said support having a particle size in the range of from 20 μm to 150 μm and a surface area in the range from 200 to 600 m^2/g ;

b) joining to the surface of said support a chromium-organic oxide to obtain a catalyst precursor,

c) subjecting said catalyst precursor to oxidising conditions to obtain the chromium in an oxidised state, and

d) impregnating said oxidised support with a metallocene compound having the formula:



wherein Cp is unsubstituted or substituted cyclopentadienyl, M is zirconium or hafnium, and X is a halide.

In a preferred embodiment of the invention the oxidised catalyst precursor obtained in step c) is subjected to reducing conditions to obtain a major part of the chromium in a bivalent oxidation state before being subjected to step d).

The catalyst defined above is used in the homopolymerization of ethylene or copolymerization of ethylene with α -olefins.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a drawing showing molecular weight distribution graphs for polyethylenes produced with the catalyst of the invention (I), and common metallocene catalysts (II) and chromium catalysts (III).

DETAILED DESCRIPTION OF THE INVENTION

The catalyst component of the present invention comprises a support to which there is joined a chromium oxide a metallocene. Suitable catalyst supports are particulate inorganic, oxygen-containing compounds, preferably selected from the group comprising silica, alumina and silica/alumina, more preferably silica.

To prepare the catalyst component this support is calcined, and subsequently an appropriate amount of a chromium compound is joined to the silica surface. Minor amounts of titanium and/or aluminium compounds may also be incorporated, either together with the chromium compound, or separately. The chromium compound

used may be any appropriate inorganic or organic chromium compound that can be oxidised to a chromium oxide. The amount of chromium compound mixed with the inorganic support must be sufficient to finally obtain between 0.001 % and 10 %, preferably from 0.1 % to 2.0 %, by weight of chromium, calculated as metallic chromium based on the weight of the inorganic support. The chromium compound may be joined to the surface of the support in various ways. Convenient methods are well known in the art and are disclosed in a number of publications, also in the patents cited hereinbefore. When the impregnation is finished any possible remaining solvent is removed to obtain a dry solid.

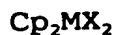
Such solid chromium oxide/silica catalyst precursors are commercially available from a number of producers. A closer description of their preparation is therefore regarded as being superfluous. Useful catalyst precursors have particle sizes preferably in the range from about 10 μm to greater than 150 μm , more preferred from 20 μm to 120 μm , and a particle size distribution from narrow to broad. The particles may be of a spherical shape obtained by the spray drying of a suspension, or having an irregular geometry obtained by comminuting a solid substance. The final catalyst component particles should have a surface area from 200 to 600 m^2/g , more preferred from 400 to 550 m^2/g , and a pore volume from 1 to 3 cm^3/g .

The obtained catalyst precursor has to be activated before use. This is done by calcination in dry air or another oxygen-containing gas at temperatures in the range from 400 to 950 $^{\circ}\text{C}$, preferably from 550 to 900 $^{\circ}\text{C}$, during a period from 10 minutes to 72 hours, preferably from 2 to 20 hours. The oxidised catalyst precursor is conventionally subjected to reduction, preferably with carbon monoxide or a mixture of carbon monoxide and an inert component, such as nitrogen or argon. The reduction is normally performed at a temperature within the range from 300 to 500 $^{\circ}\text{C}$ during a period from 5 minutes to 48 hours, preferably from 1 to 10 hours. When the reduction treatment is finished, the major part of the contained chromium should preferably be in a bivalent oxidation state. Such a reduction step is not obligatory.

Unreduced chromium oxide will eventually be reduced by the olefin monomers during polymerisation. The only drawback is that there will be observed an induction period before the chromium oxide catalyst sites start to produce polyethylenes. When the chromium oxide/silica catalyst component is in a reduced state, either as a dry powder or as a suspension in a dry oxygen-free hydrocarbon solvent, e.g. an alkane, it must be stored under inert conditions.

The present invention is not restricted to any particular procedure for the preparation of the chromium oxide/silica catalyst, and other methods than the one described here may also be applicable. Certain polymer properties will vary depending on the particular conditions applied during the preparation of the chromium catalyst component.

The obtained chromium oxide/silica catalyst is then impregnated with a cyclopentadienyl transition metal halide, in this specification termed "metallocene". Among the many different metallocenes that may be useful in the present invention, particularly preferred metallocenes can be represented by the simplified formula:



wherein Cp is an unsubstituted or substituted cyclopentadienyl compound, M is a transition metal and X is a halide. Preferably M is zirconium or hafnium, more preferred zirconium. The halide X is preferably chlorine.

A number of suitable metallocene compounds of the formula above are known in the art and have been recited in earlier patent publications (see for example WO 96/14154 mentioned above). Preferred metallocene compounds are bis-(alkylcyclopentadienyl)-transition metal halides, preferably bis-(n-butylcyclopentadienyl)-zirconium dichloride or bis-(n-butylcyclopentadienyl)-hafnium dichloride. Metallocene catalysts are often designated "single site catalyst", abbreviated SSC. A procedure for the preparation of supported metallocene catalysts is disclosed in Applicant's earlier Norwegian patent application no. NO 960898,

the description of which is included herein by reference.

The catalyst must also comprise an activator component, such as an aluminoxan or an ionic activator, preferably an aluminoxan, and most preferably methylaluminoxane (MAO). The aluminoxan may be deposited onto the activated chromium oxide/silica catalyst before, simultaneously with or after the deposition of the metallocene compound. Most conveniently both aluminoxan and metallocene are dissolved in a solvent, e.g. toluene, and the combined toluene solution is used to impregnate the chromium oxide/silica catalyst. Eventually the solvent is removed by evaporation, preferably in an inert atmosphere, whereupon the catalyst is ready for use. The final catalyst will contain both chromium, zirconium or hafnium, and aluminium. In an embodiment of the present catalyst, it contains from 0.4 % to 10 %, preferably from 0.4 % to 1 %, by weight of chromium; from 0.1 % to 0.4 %, preferably about 0.2 %, by weight of zirconium; and from 5 % to 20 %, preferably about 5 %, by weight of aluminium; calculated as metal based on the total weight of the catalyst.

The present catalyst can be used to polymerise ethylene alone, or ethylene with up to 20% by weight of a comonomer or a mixture of different comonomers. As comonomers may be used all polymerizable α -olefins of the general formula $\text{CH}_2=\text{CHR}$, wherein R is a hydrocarbon radical containing 1-18 carbon atoms, preferably 1-10 carbon atoms. Examples of particularly preferred α -olefins are propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

Polymerisations can be performed in any conventional type of reactor, such as in a batch reactor or most preferably in a continuous reactor. The present catalysts are suited for use in all types of olefin polymerisations, including gas phase and suspension polymerisations.

As used herein, the term "polyethylene" refers to both ethylene homopolymers and ethylene copolymers. The polyethylenes obtained by the process of the present invention will have a broad or bimodal molecular weight distribution (MWD), i.e. there will be

a more or less distinct tail at the low and/or high molecular weight parts of the MWD graph. In figure 1, graph I represents a typical molecular weight distribution for polyethylenes obtained by the use of the catalysts of the invention. The unique feature of the present catalysts is that they contain active chromium sites and active metallocene sites on the same catalyst particle. The chromium sites on the catalyst will behave like any Cr/SiO₂ catalyst and produce polyethylenes having a high average molecular weight and a broad MWD. A typical MWD curve representing Cr catalysed polyethylene is shown in Fig. 1 (graph III). Analogously, the metallocene sites on the catalyst will act independently of the Cr sites and produce polyethylenes having a lower average molecular weight and a narrow MWD (represented by graph II in Fig. 1). The present catalysts combine both these behaviours in one and the same catalyst particle. Thus, each polymer particle contains both Cr and metallocene polymers, and the final polymer will give a homogeneous melt when processed.

The polyethylenes produced with the catalysts of the invention will have an average molecular weight of the same magnitude as the metallocene-based polyethylenes, and a MWD of the same magnitude as the chromium-based polyethylenes. Prior to polymerisation, the catalyst may optionally be prepolymerized with a minor amount of ethylene in accordance with methods well known in the art, before being fed continuously to the polymerisation reactor. In general, polymerisations are performed at temperatures below about 110 °C, and at a total pressure in the range of up to 50 bar. Hydrogen is used to control the molecular weight and melt index of the polymer, while comonomers are used to control the branching on the polyethylene backbone and hence the density of the polyethylene. The polymerisation parameters mentioned above are well known in the art and further details concerning polymerisations should be superfluous. Typical polymerisation conditions are presented in the examples below.

The produced polyethylenes will have a density from 910 to >960

kg/m³, and a melt index from 0.01 to above 100 g/10 min, preferably from 0.1 to 60 g/10 min (determined according to the method of ASTM 1238), depending on the polymerisation conditions, as explained above. More detailed specifications concerning the properties of the obtained polyethylenes are given in the examples.

The present invention shall now be explained in more details by the following examples.

EXAMPLES

Preparation of catalysts

Cr/SiO₂ catalyst component

In the following examples three different commercially available Cr/SiO₂ catalyst precursors were used, denominated A, B and C. For comparison a support comprising silica only, denominated D, is also included. Relevant physical and chemical properties are listed in Table 1. Such catalysts are obtainable from various companies, for instance from companies Grace, Crosfield and PQ, and they represent the broadness of those Cr/SiO₂ catalyst precursors actually used today.

The calcination/activation of the catalyst precursors were carried out under fluidized bed conditions at those temperatures indicated in Table 2. Procedures well known in the art were followed. A 10 g sample of each catalyst support was activated/calcined in dry air for 5 hours to oxidise Cr to CrO₃ and reduce the concentration of surface hydroxyl. Optionally, this oxidation step was followed by reduction for 3 hours with carbonmonoxide (CO) in nitrogen (N₂), as indicated in Table 1, to reduce the oxidation state of the chromium.

TABLE 1
Cr/SiO₂ catalyst components

	A	B	C	D
Chromium (wt%)	0,5	1,0	1,0	0
Aluminium (wt%)	0,8	0	<0,3	0
Titanium (wt%)	0	2,6	2,5	0
Pore volume (ml/g)	2,5	1,0	2,5	
Surface area (m ² /g)	400	490	450	
Activation temp. in air/CO (°C)	580/380 680/380	580/-	815/- 815/380 620/380	600/-

Impregnation with a metallocene compound and MAO

All calcined components listed in Table 2 were transferred to a glove box and in a dry, oxygen-free nitrogen atmosphere impregnated with bis(n-butylcyclopentadienyl) zirconium dichloride and with methyl aluminoxane, according to the following procedure:

- 1) bis(n-butylcyclopentadienyl)zirconium dichloride is weighed into a Thomas flask equipped with a magnet bar stirrer;
- 2) 30% by weight of methyl aluminoxane (MAO) in toluene is added to the transition metal salt;
- 3) an additional amount of toluene is added and the content of the flask stirred for 30 minutes;
- 4) each catalyst support indicated in Table 3 is weighed into another Thomas flask equipped with a lid and a magnet stirrer; and
- 5) the catalyst support is stirred while the solution from step (3) is added dropwise by means of a syringe during a period from 5 to 10 minutes, thus obtaining a free flowing, not saturated powder, free from any lumps,
- 6) the stirring of the impregnated powder is continued for another 30 minutes, and subsequently

- 7) the lid on the flask is punctured with two cannula and a nitrogen purge established through the space inside the flask for about 30 minutes, and
- 8) the dried catalyst is stored under nitrogen until use.
- Experimental parameters are given in Table 2.

TABLE 2
Catalysts

Catalyst	Catalyst precursor (g)	Zr compound (g)	MAO (ml)	Toluene (ml)
A	3,00	0,033	3,57	3,63
B	2,00	0,022	2,38	0
C	3,00	0,033	3,57	3,93
D	3,40	0,037	3,90	1,20

General polymerisation procedures

A laboratory stainless steel batch reactor equipped with a paddle stirrer was heated to 80 °C to 100 °C and purged with nitrogen, before a specific amount of catalyst was introduced, then isobutan was added and the stirring started. The temperature was adjusted to the desired temperature and ethylene fed to the reactor (with or without hydrogen) until a predetermined pressure was reached. Ethylene was then polymerised. The overall pressure was kept constant during the entire polymerisation run by feeding ethylene. The ethylene consumption was monitored during the polymerisation. When hexene-1 was used as a comonomer, this was fed to the reactor together with the isobutane. Optionally, also minor amounts of hydrogen were added to the reactor blended with the ethylene feed. All reagents used was of "polymerisation grade".

Hexene-1, when used, was fed to the reactor by the use of a pump working in cascade with the ethylene feeding system. The reactor temperature was kept constant at a fixed temperature to an accuracy of $\pm 0,2$ °C by automatically adjusting heating and/or

cooling of the reactor. The polymerisation run was stopped when a desired polymer yield had been reached, or after a preset polymerisation time. The obtained polymer was weighed and samples collected for further treatment and measurements. One major sample was mixed with an additive-containing masterbatch to stabilise the polymer prior to further treatments.

Reactor conditions for the polymerisations are presented in Tables 4 to 8.

Polymer characterisation methods

The properties of the obtained polymers were determined by the use of the following characterisation methods:

Melt index Melt indices, MFR, were determined according to the method of ASTM D 1238 at 190 °C and loads of 2.16 kg and 21.6 kg. The ratio between the melt index obtain with 2.16 kg and 21.6 kg loads is reported as FRR.

Rheology The relation between the molecular weight (Mw) determined by gel permeation chromatography (GPC) and zero viscosity (η_0) determined by dynamic measurements is expressed by the well known equation:

$$\eta_0 = K(Mw)^{3.4}$$

where K is a proportional constant. Because zero viscosity often is difficult to calculate $\eta(0.05)$ is used instead. Thus, a high $\eta(0.05)$ value means high molecular weight. Polymers with a broad molecular weight distribution (MWD) have a more pronounced shear thinning compared to polymers with a narrow MWD. Thus, polymers with broad MWD will have a low $\eta(300)$ value.

Cole-cole plot The modulus of rigidity, G^* , is given as: $G^* = G' + iG''$. The real part, the storage modulus G' , expresses the elasticity of the polymer while the imaginary part, the loss modulus G'' , expresses the viscous part of the polymer. A more elastic polymer then gives higher G' values than a less elastic polymer. A plot of G'/freq versus G''/freq gives information about the elasticity of polymers. Therefore, such a plot gives information about possible two phase structures: The curves then have two areas in the plot where they have different shapes.

Polydispersity Index The polydispersity index, PI, given by the expression: $PI = 10^5/x$, wherein x is the value on the abscissa at the point of intersection between G' and G'' , is a function of among other things M_w and MWD . When the G' curve has a higher slope, the point of intersection will take place at a smaller x value and PI will increase, i.e. more elastic polymers (that means polymers with broader MWD) give higher PI values.

Gel Permeation Chromatography Gel Permeation Chromatography, GPC, was used to separate molecules according to their sizes and to calculate M_w , M_n and MWD .

Infrared Analysis Infrared analyses, IR, in the area 1250 to 890 cm^{-1} was used to detect end groups and the comonomer distribution in the polymers. Polyethylenes produced with chromium catalysts will have unsaturated vinyl end groups, while metallocene catalysts produces trans-vinylene end groups, and thus the fraction of polyethylenes produced from each catalyst can be quantified.

Examples 1 and 2

In an 8 l stainless steel reactor ethylene with 0.2% by weight of hexene was polymerised at 80 °C (example 1) and at 94 °C (example 2) in the presence of catalyst A specified above, according to the general polymerisation procedure described above. Experimental parameters and polymerisation results are presented in Tables 4 and 5. They reveal that the polymerisation temperature had little influence on the activity of the catalyst.

Example 3

The polymerisation procedure of Example 1 was repeated, except that the chromium on the catalyst was in an oxidised state (not reduced). Experimental parameters and polymerisation results are presented in Tables 4 and 5. The polymerisation activity was low.

Example 4 (Comparative)

The catalyst used was a chromium oxide catalyst not impregnated with metallocene and aluminoxan. The procedure of Example 2 was repeated. Experimental parameters and polymerisation results are

presented in Tables 4 and 5. The activity of the catalyst was low.

Example 5 (Comparative)

The polymerisation procedure of Example 1 was repeated, except that the catalyst used was a conventional metallocene catalyst (SSC). Experimental parameters and polymerisation results are presented in Tables 4 and 5. The activity of the catalyst was low.

Example 6 (Comparative)

The polymerisation procedure of Example 2 was repeated with a catalyst not containing metallocene. The catalyst had the same specifications as the catalyst of examples 1 and 2, except that ~~the chromium oxide/silica catalyst had not been impregnated with~~ metallocene, only with MAO. The activity of the catalyst was very low.

The catalyst of the present invention used in examples 1 and 2 had a significant higher activity than the common metallocene (single site) catalyst of comparative example 5, and the common chromium catalyst of comparative example 4. The catalyst of comparative example 6, which was not impregnated with metallocene, had a very low activity. The dual site catalysts of the present invention seem to contain an increased amount of active polymerisation sites in comparison with the other catalysts. The activity of the catalyst of the present invention is higher than the combined activities of the catalysts used in comparative examples 5 and 6. Consequently, the combined dual site catalyst of the present invention will have a synergistic effect.

The results from the characterisations of the obtained polyethylenes presented in Table 5 show that the polymers obtained with the catalyst of the present invention (examples 1 and 2) have properties laying between those of polyethylenes obtained with a normal chromium catalyst (comparative example 4) and a normal metallocene catalyst (comparative example 5). This supports the

assumption that both the metallocene and chromium sites on the catalysts of the present invention are active during the polymerisation. Also the molecular weights confirm this. The polyethylenes obtained with the dual site catalyst have an increased Mw and MWD compared with the metallocene based catalysts (comparative example 5) and reduced Mw and MWD compared with the chromium based catalyst (comparative example 4).

IR analyses of films made from the obtained polymers detect the fraction of polymers polymerised from the metallocene sites on the catalysts. The results presented in Table 5 supports that both the metallocene and chromium sites are active during polymerisations. It is obvious that the dual site catalysts of the present invention produces two different polyethylenes simultaneously.

TABLE 4
Polymerisation's with various catalysts

Examples	1	2	3	Comp. 4	Comp. 5	Comp. 6
Catalyst No.	A	A	A ²⁾	CrO ₃ ³⁾	SSC	Cr/MAO ⁴⁾
Cr/SiO ₂ activation						
Oxidation temp. (°C):	680	680	680	680	600(1)	680
Reduction temp. (°C):	380	380	not red.	not red.	not red.	380
Polymerisation						
Reactor temp. (°C)	80	94	80	94	80	94
Total pressure (baro)	26,0	30,5	26,0	30,5	26,0	30,5
Cat. weight (g):	0,649	0,653	0,888	0,412	0,798	0,892
Induction time (min):	0	0	1	5	0	1,5
Run time (min):	72	78	96	173	78	173
Polymer yield (g):	1820	1850	980	1265	1630	1010
Productivity (g/g):	2810	2830	1000	3070	2040	1130
Activity (g/g·hr):	2370	2280	680	1200	1540	400

- (1) = Silica support calcination
 (2) = Chromium oxide not reduced
 (3) = CrO₃ only
 (4) = No impregnation with metallocene

TABLE 5
Characterisation of Polyethylenes

Ex. No.	1	2	3	Comp. 4	Comp. 5	Comp. 6
MFR2	0,43	0,60	0,12	0,03	0,96	<0,01
MFR21	10,2	15	5,5	2,8	16,5	1,4
FRR	17,2	25	46	90	17,2	>140
Density	947	948	947	953	946	947
G'(0,05)	404	305	2140	5829	11	11320
$\eta(0,05)$	17563	13801	66701	182780	7696	323525
$\eta(300)$	1353	1168	1431	1323	1412	1533
PI	0,5	0,6	0,8	4,5	0,4	7,7
Cole-cole plot	Two Phases	Two Phases	nd	One Phase	One Phase	One Phase
M _w	160,000	140,0000	200,000	nd	135,000	nd
M _n	45,000	44,000	41,000	nd	53,000	nd
MWD	3.6	3.2	4.9	nd	2.5	nd
§SSC polymer	82	55	33	nd	100	nd

nd = not determined

Examples 7 to 12

Polymerisation's of ethylene in the presence of catalyst A were performed in a 2 l stainless steel reactor with 1 l isobutane as the reaction medium containing 0.16 % or 2.92 % by weight of hexene as comonomer. The ethylene feed contained 0, 1270 or 7000 ppm(mole) of hydrogen. The polymerisations were allowed to proceed for 60 min and were then terminated. The experimental parameters and polymerisation results are specified in Table 6.

Examples 13 and 14 (Comparative)

The polymerisation procedure of Examples 7 to 12 was followed. The catalyst used was a common metallocene catalyst. Experimental parameters and polymerisation results are presented in Table 6.

Table 6 shows that a polymerisation temperature of 94 °C compared with 85 °C gives polyethylenes with a higher Mw, a broader MWD and a distinct tail on the MWD curve. The reason is that chromium sites will have increasing activities as the temperature increases. The polyethylenes have also two-phase structures on cole-cole plots.

The influence of a lower chromium oxidation temperature on the catalytic activity can be seen by comparing example 10 (oxidation temperature 580 °C) with example 8 (oxidation temperature 680 °C). The polyethylene in example 10 has a lower melt index, but otherwise the differences are small. Polyethylenes produced with a high concentration of 7000 ppm hydrogen in the ethylene feed will have a higher Mw when polymerised with the dual site catalyst of the present invention (example 11) than when polymerised with a conventional metallocene catalyst (comparative example 14). The catalysts of the invention will also give a broader MWD and a tail on the MWD curve.

TABLE 6

Examples	7	8	9	10	11	12	Comp. 13	Comp. 14
Catalyst Ref. No.	A	A	A	A	A	A	SSC	SSC
Oxidation temp. (°C):	680	680	680	580	680	680	600	600
Reduction temp. (°C):	380	380	380	380	380	380	NA	NA
C6 in iC4 (wt%):	0.16	0.16	2.92	0.16	2.92	2.92	0.16	2.92
H2 in C2 (mol ppm):	0	1270	1270	1270	7000	0	1270	7000
Reactor temp. (°C)	94	94	85	94	94	94	94	94
Total pressure (baro)	30.5	30.5	22.0	30.5	25.0	25.0	30.5	25.0
Cat. weight (g):	0.094	0.090	0.130	0.119	0.142	0.104	0.093	0.099
Productivity (g/g):	1800	1330	1540	1200	1110	1590	3060	2830
Activity to P4000 (g/g-hr):	2000	1700	1670	1420	1270	1850	3220	3110

TABLE 6 (cont.)

Examples	7	8	9	10	11	12	Comp. 13	Comp. 14
MFR2 (g/10 min):	1,3	26,6	25	18,4	>80	1,8	16,8	>100
MFR21 (g/10 min):	24					35		
Density (g/dm ³)	946	957	930	955		930	956	932
FRR 21/2	18,5					19,4		
G'0,05	30	93	0,5		570	4		
η 0,05	6080	3590	330		25500	500		
η 300	1250	200	210		1140	270		
PI	0,41	nd	nd		0,72	nd		
M _w	135000	220000	55000	195000	30000	115000	60000	10000
M _n	38000	9200	19000	12000	4000	26000	15000	3000
M _w /M _n	3,6	24	2,9	16,3	7,5	4,4	4	3,3
Cr/SSC	5/95	60/40	10/90	50/50	nd	10/90		

nd = not determined

MFR determined with powder

Examples 15 and 16

The catalyst B specified in Tables 1 to 3 calcined at 585 °C and then reduced at 380 °C before being impregnated with the metallocene catalyst and aluminoxan, as described above, was used in the polymerisations of ethylene in a 2 l stainless steel autoclave by following the general polymerisation procedure described above. The reaction medium was 1 l isobutane which contained hexene-1 as comonomer in amounts of 0.16 or 2.92% by weight, respectively, while the ethylene contained 270 ppm (moles) of H₂. The polymerisations were terminated after 60 minutes. Experimental parameters and polymerisation results are presented in Table 7.

Example 17 (Comparative)

The polymerisation procedure of Example 15 was followed, except that the catalyst used was a single site metallocene catalyst on a silica support. Experimental parameters and polymerisation results are presented in Table 7.

Catalyst B is a Cr/SiO₂ catalyst having a low pore volume, which is often used for the production of polyethylenes of high Mw. Examples 15 and 16 show that dual site catalysts also can be obtained with low pore catalyst precursors and give catalysts of acceptable activity. The melt index of the final polyethylene was controlled by the use of hydrogen, and the density by the use of hexene-1. Even if the obtained MWD is narrow, the MWD curve has a tail indicating a bimodal MWD. The influence of the chromium sites is less pronounced here than in the previously reported catalyst A.

TABLE 7

Examples	15	16	17
Catalyst Ref. No.	B	B	SSC
Oxidation temp. (°C):	585	585	600
Reduction temp. (°C):	380	380	-
C6 in iC4 (wt%):	0,16	2,92	0,16
H2 in C2 (mol ppm):	1270	1270	1270
Reactor temp. (°C)	85	94	94
Total pressure (bar)	27,5	25,0	30,5
C2 pressure (bar)	11,7	6,2	11,7
Cat. weight (g):	0,139	0,094	0,093
Productivity (g/g):	1550	1810	3060
Activity to P4000 (g/g·hr):	1530	2000	3220
MFR2 (g/10 min):	22	22,8	16,8
MFR21 (g/10 min):	nd	nd	nd
Density (g/dm ³)	953	933	956
Rheology:			
G'0,05	2,9	4,1	4,0
η 0,05	570	660	500
η 300	240	250	270
Two-Phase struc.	Yes	Yes	No
Mw	70000	-	60000
Mn	15000	-	15000
Mw/Mn	4,7	-	4,0
Cr/SSC	1/9	1/9	

nd = not determined

Examples 17 to 23

The catalyst C specified in Tables 1 to 3 calcined at 815 °C and then reduced at 380 °C (examples 17 to 20), and not reduced (examples 21 to 23), before being impregnated with the single site metallocene catalyst and aluminoxan, as explained in detail above, was used in the polymerisation of ethylene at polymerisation conditions given in Table 8, where also the polymerisation results are presented.

Examples 24 and 25

The procedure of Examples 17 to 20 was repeated, except that catalyst C was activated at a lower temperature of 620 °C. Experimental parameters and polymerisation results are presented in Table 8.

Example 26 (Comparative)

The procedure of Example 23 was repeated, except that the catalyst was a normal single site metallocene catalyst. Experimental parameters and polymerisation results are presented in Table 8.

All catalysts used in examples 17 to 25 gave polyethylenes having a high Mw and broad MWD. Cole-cole plots indicate two-phase structures, and the GPC curves show tails at both low and high Mw. These catalysts C gave polyethylenes with higher molecular weights than the catalysts A. In comparison, by the use of a common metallocene catalysts based on catalyst precursor C (comparative example 26) it was obtained polyethylenes with a more narrow MWD and no tails on the MWD curve. The catalysts of examples 17 to 25 are all dual site catalysts having acceptable activities. These examples show that it is possible to obtain dual site catalysts also without subjecting the chromium to reduction.

TABLE 8

Examples	17	18	19	20	21	22	23	24	25	Comp. 26
Catalyst Ref. No.	C	C	C	C	C	C	C	C	C	SSC
Oxidation temp. (°C):	815	815	815	815	815	815	815	620	620	600
Reduction temp. (°C):	380	380	380	380	not red.	not red.	not red.	380	380	
C6 in iC4 (wt%):	0,16	0,16	2,92	2,92	0,16	0,16	5,96	2,92	2,92	5,96
H2 in C2 (mol ppm):	0	1270	0	1270	0	0	0	1270	0	0
Reactor temp. (°C)	94	85	85	94	94	94	85	85	94	85
Total pressure (baro)	30,5	27,5	22,0	25,0	30,5	30,5	19,5	22,0	25,0	19,5
Cat. weight (g):	0,796	0,126	0,146	0,139	0,120	0,568	0,609	0,135	0,119	0,567
Induction time (min):	1	2	0	1	0	0	1	0	0	0
Run time (min):	56	60	60	60	60	56	56	60	60	42
Polymer yield (g):	1110	130	178	176	360	1400	610	224	205	1420
Productivity (g/g):	1400	1030	1220	1270	3000	2500	1000	1620	1720	2600
Activity to P4000 (g/g-hr):	1280	1200	1300	1370	3290	3000	1100	1800	1780	3160

nd = not determined

TABLE 8 (cont.)

Examples	17	18	19	20	21	22	23	24	25	Comp. 26
MFR2 (g/10 min):	0,77	8,1	1,3	16,4	0,32	0,40	1,10	21,4	1,50	1,10
MFR21 (g/10 min):	16	>290	30	nd	15	16	22	nd	30	17,5
FRR21/2	20,8	>25	23		47	40	20		20	15,9
Density:	942	955	926	933	951	951	915	934	925	912
G'0,05	290	332	31	8	980	110	139	5,5	14	16
η 0,05	16700	11090	5580	790	39900	7500	11090	530	5260	6720
η 300	1200	280	1150	210	1000	890	1030	200	1260	1390
PI	0,59		0,44		1,23	0,55	0,64			0,42
Two Phase Structure	Yes		Yes	Yes	Yes	Yes	Yes	Yes		
Mw	190000	225000	145000	80000	200000	190000	168000	78000	120000	120000
Mn	20000	10000	20000	10000	15000	15000	12000	16000	27000	40000
Mw/Mn	9,5	23	7,3	8,0	13,3	12,7	14	4,9	4,4	3
Cr/SSC	20/80	50/50	1/9	1/9	65/35	60/40	30/70	1/9	1/9	

nd = not determined

Example 27

In a stainless steel reactor was filled 1.8 l isobutane and 20 ml 1-hexene. The reaction medium was heated to 90 °C and ethylene fed until a pressure of 5 bar. Catalyst A from Table 1, activated at conditions 680-380 °C, was introduced and the polymerisation started immediately. After 60 minutes polymerisation time the polymerisation reaction was terminated and the produced polyethylene recovered. Experimental parameters and polymerisation results are presented in Table 9.

Example 28

The procedure of Example 27 was repeated, except that the catalyst used contained hafnium instead of zirconium. Thus, the metallocene impregnated onto the chromium oxide/silica catalyst was bis(n-butylcyclopentadienyl)hafnium dichloride. The catalyst had the same greenish colour as the catalyst used in Example 27. Experimental parameters and polymerisation results are presented in Table 9.

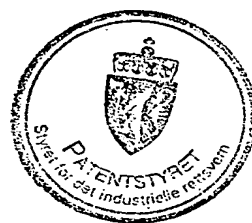
Example 29 (Comparative example)

The procedure of Example 27 was repeated, except that the catalyst used had not been impregnated with metallocene. Thus, the catalyst was a chromium oxide/silica catalyst. Experimental parameters and polymerisation results are presented in Table 9.

TABLE 9

Examples	27	28	Comp 29
Catalyst Ref. No.	A, Zr	A, Hf	CrO _x
Oxidation temp. (°C):	680	680	680
Reduction temp. (°C):	380	380	380
C6 in iC4 (wt%):	1.1	1.1	1.1
Cat. weight (g):	0,110	0,202	0,144
Activity (g/g·hr):	1180	250	310
MFR2 (g/10 min):	3.6	nd	0.21
MFR21 (g/10 min):	60	0.78	7.9
Density (g/dm ³)			
G'5kPa (Pa)	575	1410	3380
η ₃₀₀ (Pa·s)	2465	400,000	218,000
Mw	92,300	381,500	203,500
Mw/Mn	2.5	3.4	12.0

nd = not determined



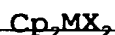
P a t e n t c l a i m s

1. A catalyst component for the polymerisation of ethylene and ethylene with α -olefins, characterised by comprising:

a) a support being a particulate inorganic oxide selected from the group comprising silica, alumina, and a combination thereof, said support having a particle size in the range of from 20 μm to 150 μm and a surface area from 200 to 600 m^2/g ;

b) a chromium oxide in an amount of from 0.001 % to 10 % by weight calculated as chromium, based on the weight of the inorganic support; and

c) a metallocene compound of formula:



wherein Cp is unsubstituted or substituted cyclopentadienyl, M is zirconium or hafnium, and X is a halide.

2. A catalyst component according to claim 1, characterised in that said particulate inorganic oxide is silica.

3. A catalyst component according to claim 1, characterised in that the chromium is mainly in a bivalent oxidation state.

4. A catalyst component according to claim 1, characterised in that the metal M is zirconium and X is chlorine.

5. A catalyst for the polymerisation of ethylene and ethylene with α -olefins, characterised by comprising the catalyst component of claims 1 to 4, and an aluminoxane.

6. A catalyst according to claim 5, characterised in that the aluminoxane is methylaluminoxane.

7. A catalyst according to claim 5, characterised in that the catalyst contains 0.4 to 10 % by weight of Cr; 0.1 % to 0.4 % by weight of Zr; and 5 % to 20 % by weight of Al; calculated as metals based on the total weight of the catalyst.

8. A catalyst according to claim 7, characterised in that the catalyst contains 0.4 to 1 % by weight of Cr, about 0.2 % by weight of Zr, and about 5 % by weight of Al.

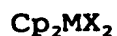
9. A method for the preparation of a catalyst component for the polymerisation of ethylene, optionally with α -olefins, characterised by comprising the steps of:

a) calcining a support being a particulate inorganic oxide selected from the group comprising alumina, silica and a combination thereof, said support having a particle size in the range of from 20 μm to 150 μm and a surface area from 200 to 600 m^2/g ;

b) joining to the surface of said support a chromium-organic compound to obtain a catalyst precursor,

c) subjecting said catalyst precursor to oxidising conditions to obtain the chromium in an oxidised state, and

d) impregnating said oxidised support with a metallocene compound having the formula:



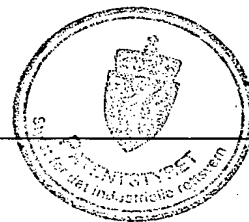
wherein Cp is unsubstituted or substituted cyclopentadienyl, M is zirconium or hafnium, and X is a halide.

10. The method of claim 9, characterised in that said catalyst has the shape of spherical or spheroidal particles.

11. The method of claim 9, characterised in that said oxidised catalyst precursor obtained in step c) subsequently is subjected to reducing conditions to obtain a major part of the chromium in a bivalent oxidation state before being subjected to step d).

12. The method of claim 9, characterised in that the amount of the organo-chromium compound used in step b) and the amount of the metallocene compound used in step d) are such that the ratio between active chromium and metallocene sites in the final catalyst is in the range from 95:5 to 5:95, respectively.

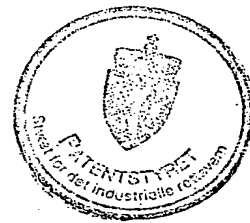
13. A use of the catalysts of claims 5 to 12 in the homopolymerisation of ethylene or copolymerisation of ethylene with α -olefins.



ABSTRACT

1/h

A catalyst component for the polymerisation of ethylene, optionally with α -olefins, comprising: a) an inorganic support b) a chromium oxide in an amount of from 0.001 % to 10 % by weight calculated as chromium; and c) a metallocene compound of formula Cp_2MX_2 , wherein Cp is unsubstituted or substituted cyclopentadienyl, M is zirconium or hafnium, and X is a halide. A catalyst is obtained by combining said catalyst component with an aluminoxan. A method for the preparation of said catalyst component comprises the steps of: a) calcining said inorganic support, b) joining to the surface of said support a chromium-organic compound to obtain a catalyst precursor, c) subjecting said catalyst precursor to oxidising conditions to obtain the chromium in an oxidised state, and d) impregnating said oxidised support with said metallocene compound.



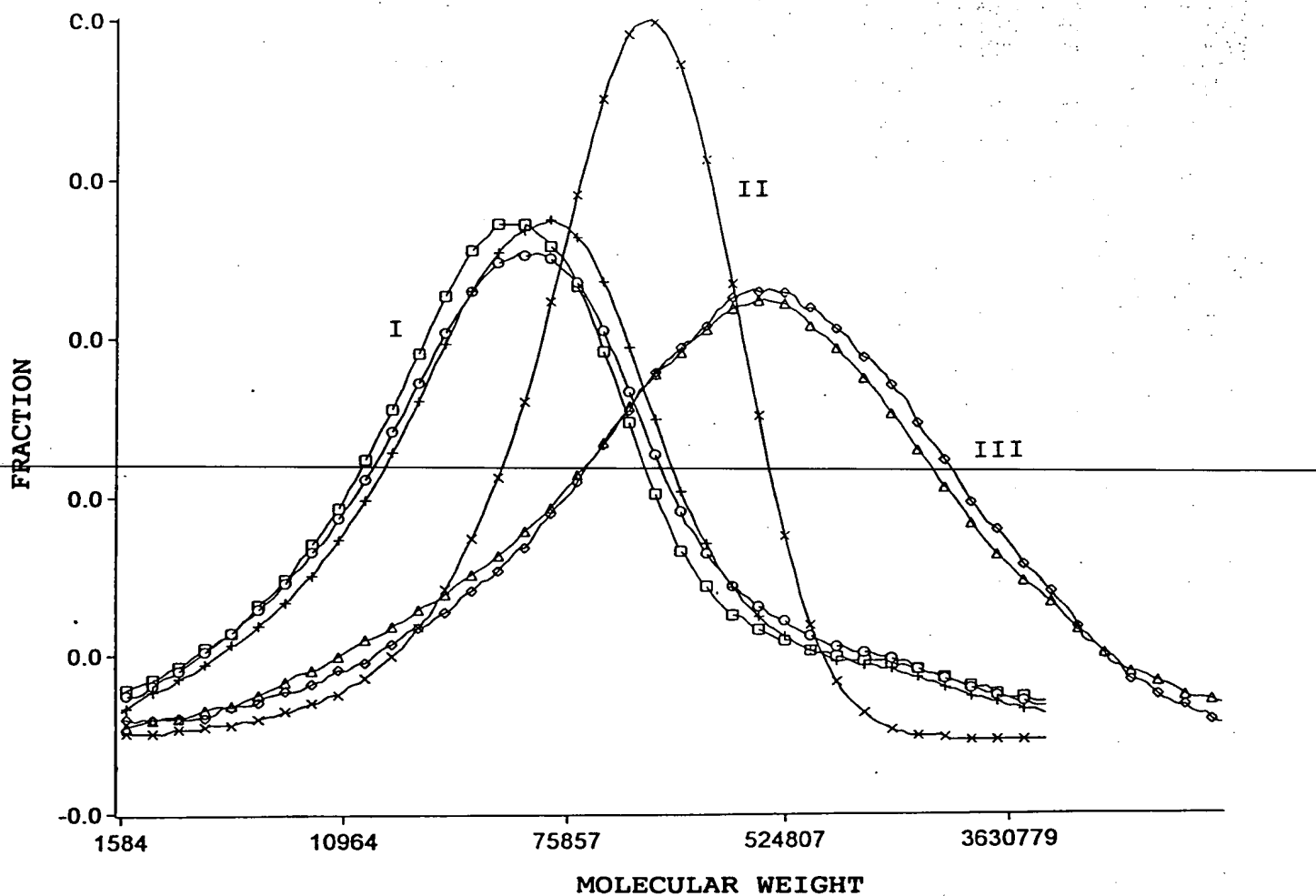


FIG. 1

